

Supporting Information

for

Kinetic investigation on tetrakis(4-sulfonatophenyl)porphyrin J-aggregates formation catalyzed by cationic metallo-porphyrins

Ilaria Giuseppina Occhiuto¹, Roberto Zagami², Mariachiara Trapani², Maria Angela Castriciano², Andrea Romeo^{1,2}, Luigi Monsù Scolaro^{1,2*}

¹ Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, University of Messina and C.I.R.C.M.S.B V.le F. Stagno D'Alcontres, 31 - 98166 Messina, Italy

² CNR - ISMN Istituto per lo Studio dei Materiali Nanostrutturati c/o Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, University of Messina, V.le F. Stagno D'Alcontres, 31 - 98166 Messina, Italy

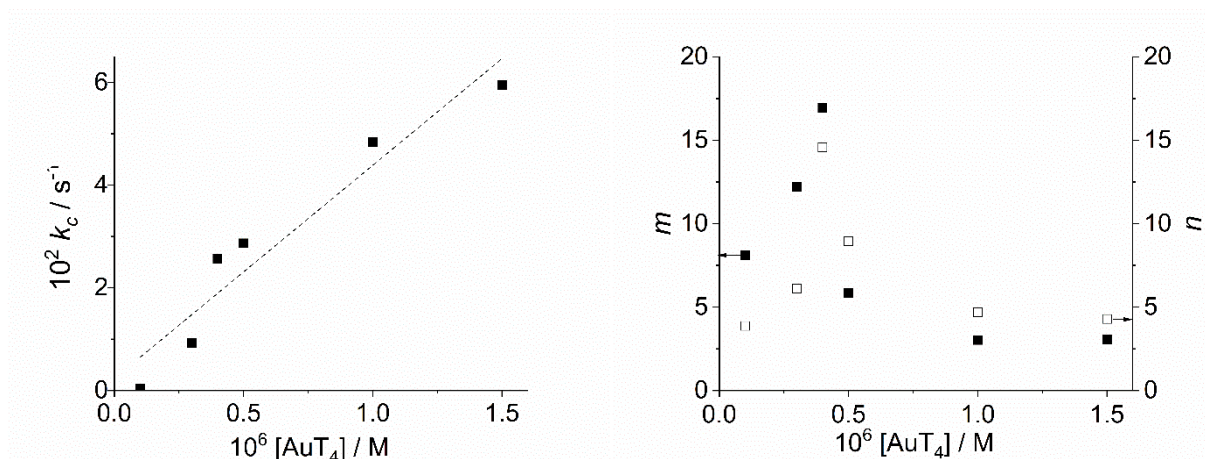


Figure S1. Plot of the autocatalytic rate constants k_c (s^{-1}) (left), and the values of m (full squares) and n (empty squares) for the aggregation of TPPS₄ as function of $[\text{AuT}_4]$ (right). (Experimental conditions: $[\text{TPPS}_4] = 3 \mu\text{M}$; $[\text{HCl}] = 0.00158 \text{ M}$, $T = 298 \text{ K}$). The lines represent the linear best fits to the experimental k_c data to the equation: $k_c = (2.34 \pm 4.72) \times 10^{-3} + (4.15 \pm 0.60) \times 10^{-2} \times [\text{AuT}_4]$.

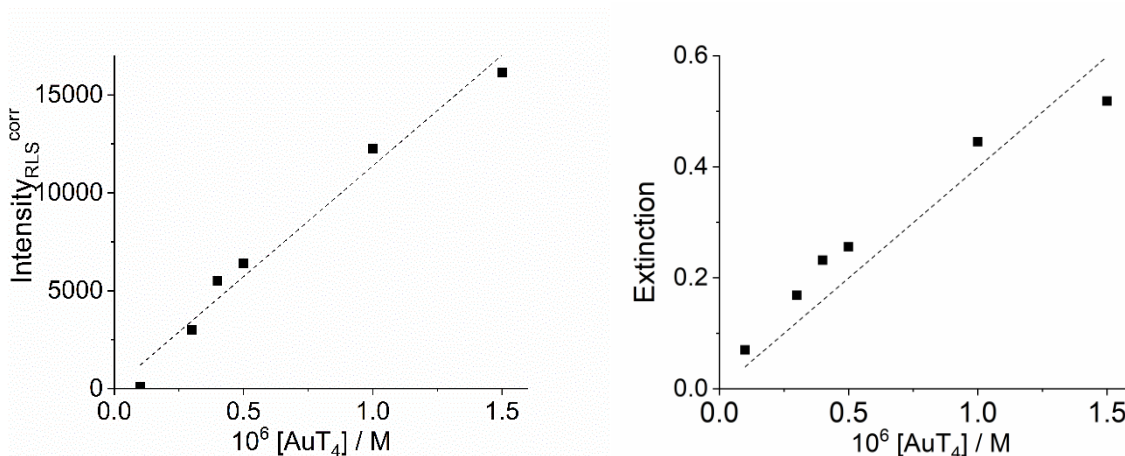


Figure S2. Intensity of RLS spectra corrected for extinction (left) and extinction of the samples (right) at the end of the TPPS₄ aggregation process catalyzed by AuT_4 as function of the concentration of this metal derivative (Experimental conditions: $[\text{TPPS}_4] = 3 \mu\text{M}$; $[\text{HCl}] = 0.00158 \text{ M}$, $T = 298 \text{ K}$). The lines represent the linear best fits to the experimental data (a: $I_{\text{RLS}}^{\text{corr}} = 10^4 \times (0.071 \pm 0.071) + 10^4 \times (1.130 \pm 0.089) \times [\text{AuT}_4]$; b: $\text{Ext} = (0.005 \pm 0.002) + (0.399 \pm 0.033) \times [\text{AuT}_4]$).

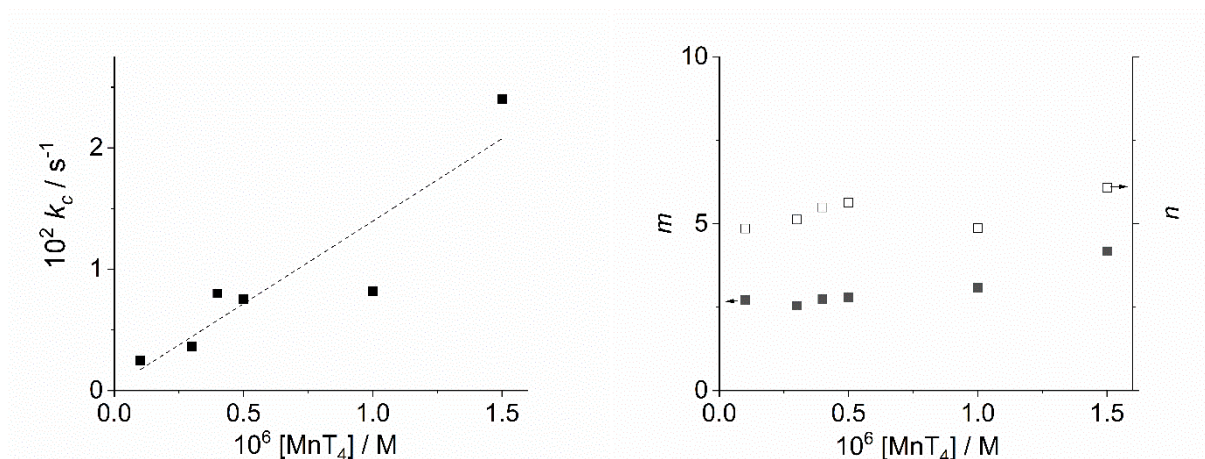


Figure S3. Plot of the autocatalytic rate constants k_c (s^{-1}) (left), and the values of m (full squares) and n (empty squares) for the aggregation of TPPS₄ as function of $[MnT_4]$ (right). (Experimental conditions: $[TPPS_4] = 3 \mu M$; $[HCl] = 0.00158 M$, $T = 298 K$). $k_c = (0.36 \pm 2.41) \times 10^{-3} + (1.36 \pm 0.30) \times 10^{-2} \times [MnT_4]$.

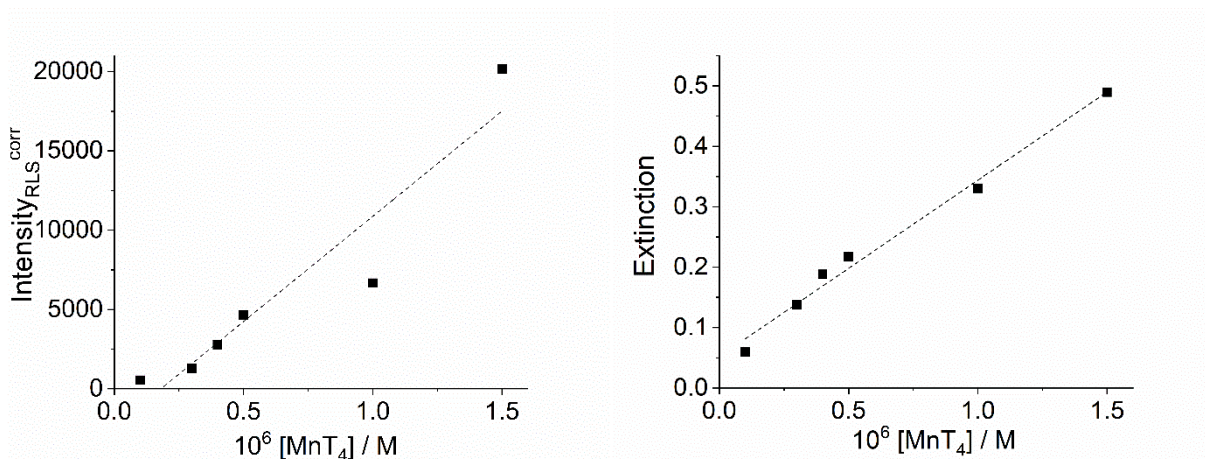


Figure S4. Intensity of RLS spectra corrected for extinction (left) and extinction of the samples (right) at the end of the TPPS₄ aggregation process catalyzed by MnT_4 as function of the concentration of this metal derivative (Experimental conditions: $[TPPS_4] = 3 \mu M$; $[HCl] = 0.00158 M$, $T = 298 K$). The lines represent the linear best fits to the experimental data (a: $I_{RLS}^{corr} = 10^4 \times (-0.239 \pm 0.179) + 10^4 \times (1.327 \pm 0.226) \times [MnT_4]$; b: $Ext = (0.052 \pm 0.013) + (0.292 \pm 0.016) \times [MnT_4]$).

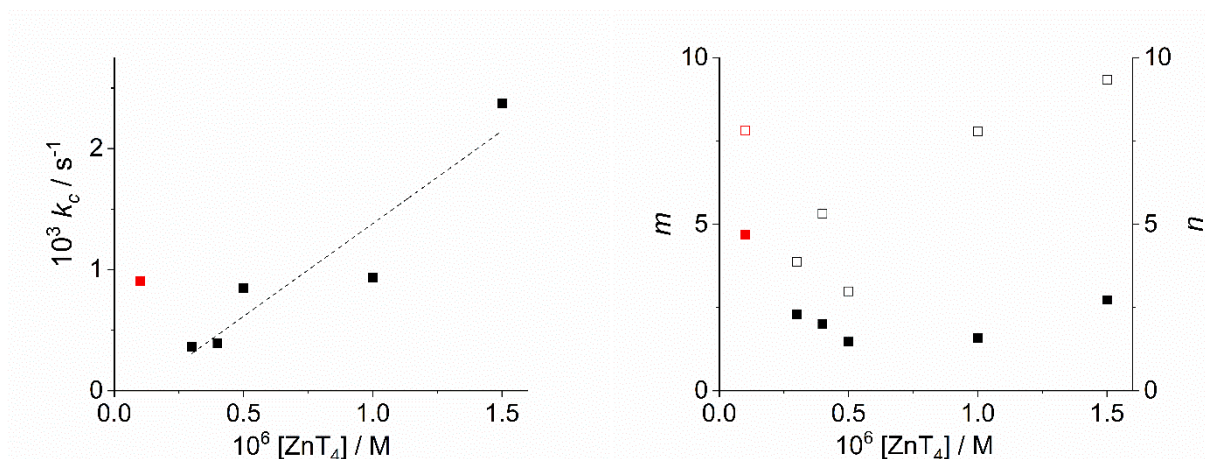


Figure S5. Plot of the autocatalytic rate constants k_c (s^{-1}) (left), and the values of m (full squares) and n (empty squares) for the aggregation of TPPS₄ as function of $[\text{ZnT}_4]$ (right). (Experimental conditions: $[\text{TPPS}_4] = 3 \mu\text{M}$; $[\text{HCl}] = 0.00158 \text{ M}$, $T = 298 \text{ K}$). $k_c = (-0.15 \pm 0.281) \times 10^{-3} + (1.53 \pm 0.32) \times 10^{-3} \times [\text{ZnT}_4]$.

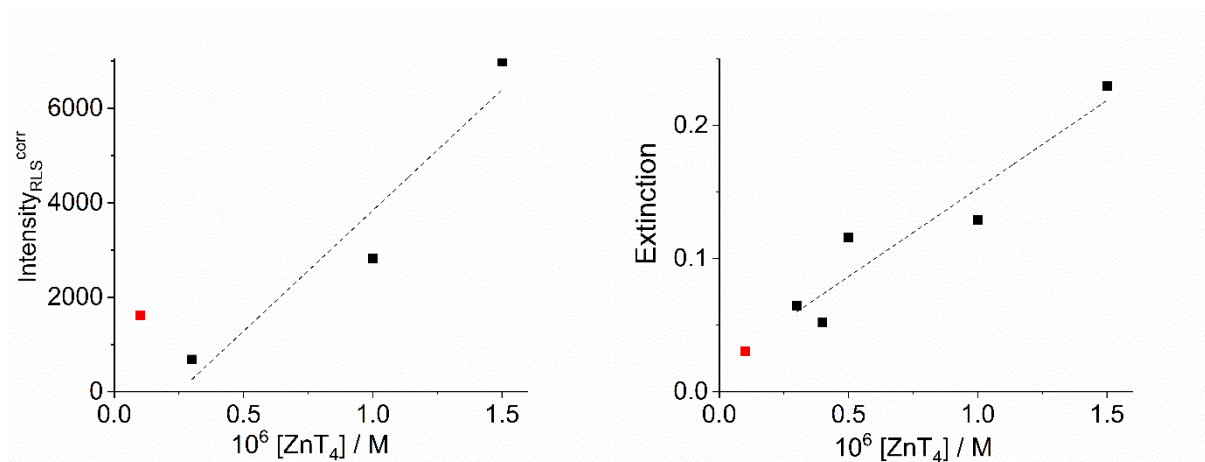


Figure S6. Intensity of RLS spectra corrected for extinction (left) and extinction of the samples (right) at the end of the TPPS₄ aggregation process catalyzed by ZnT_4 as function of the concentration of this metal derivative (Experimental conditions: $[\text{TPPS}_4] = 3 \mu\text{M}$; $[\text{HCl}] = 0.00158 \text{ M}$, $T = 298 \text{ K}$). The lines represent the linear best fits to the experimental data (a: $I_{\text{RLS}}^{\text{corr}} = 10^4 \times (-0.127 \pm 0.154) + 10^4 \times (0.511 \pm 0.146) \times [\text{ZnT}_4]$; b: $\text{Ext} = (0.020 \pm 0.022) + (0.132 \pm 0.026) \times [\text{ZnT}_4]$).

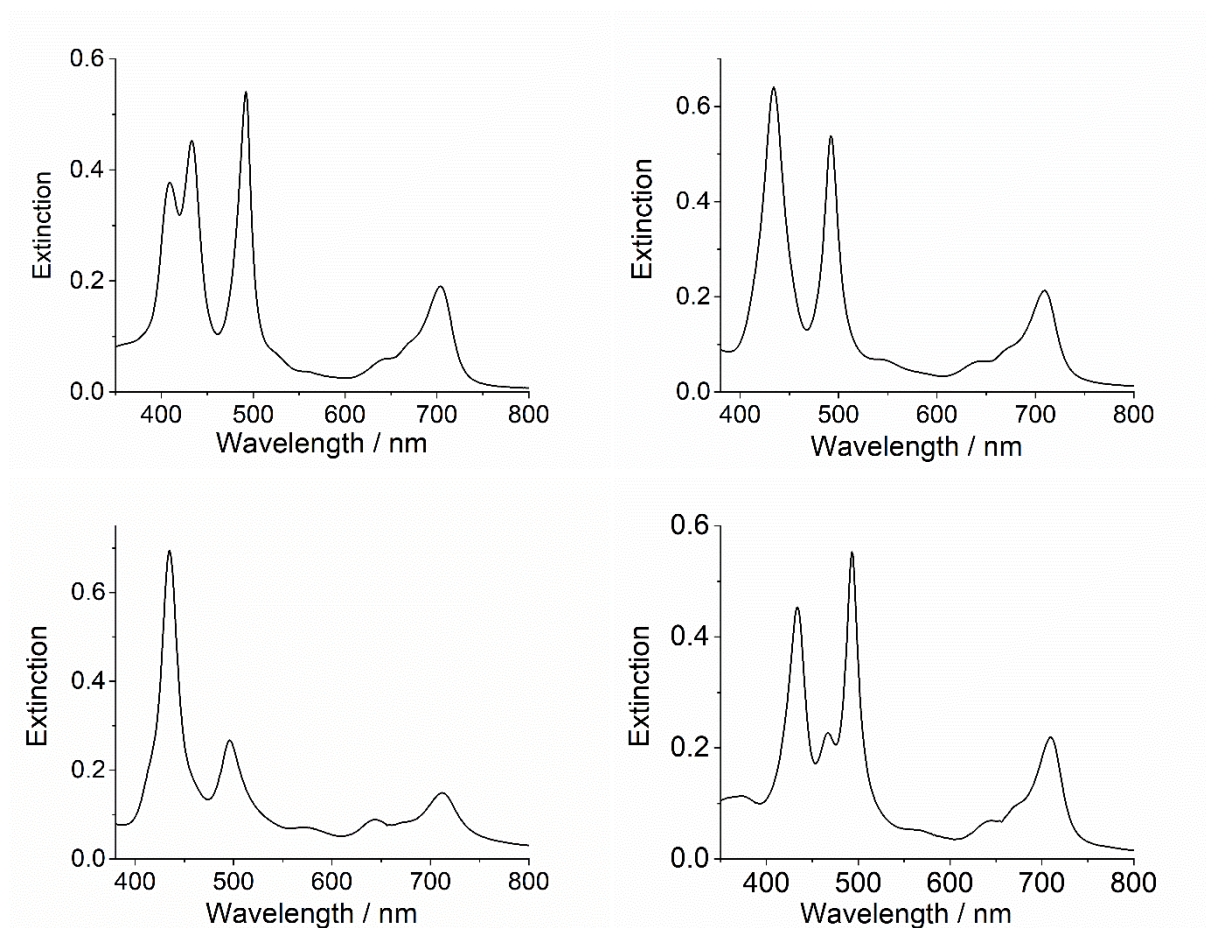


Figure S7. UV/Vis extinction spectra of TPPS₄ J-aggregates in the presence of AuT₄ (upper left), of CoT₄ (upper right), of ZnT₄ (lower left), of MnT₄ (lower right). (Experimental conditions: [TPPS₄] = 3 μ M; [MT₄] = 1.5 μ M; [HCl] = 0.00158 M, T = 298 K).

Table S1. Relevant kinetic parameters for TPPS₄ aggregation in J-aggregates (k_c , m and n) as function of [MT₄]

	$10^6 \times [\text{MT}_4] / \text{M}$	$10^3 \times k_c / \text{s}^{-1}$	m	n
Au	0.1	0.34 ± 0.02	8.1 ± 0.3	3.9 ± 0.1
	0.3	9.27 ± 0.25	12.2 ± 1.0	6.1 ± 0.5
	0.4	25.7 ± 0.1	16.9 ± 7.2	14.6 ± 6.9
	0.5	28.7 ± 0.1	5.9 ± 1.1	8.9 ± 2.0
	1.0	48.4 ± 0.1	3.0 ± 0.1	4.7 ± 0.2
	1.5	59.5 ± 0.2	3.1 ± 0.1	4.3 ± 0.2
Co	0.1	3.02 ± 0.02	2.3 ± 0.1	4.5 ± 0.2
	0.3	6.92 ± 0.02	2.3 ± 0.1	4.6 ± 0.1
	0.4	10.3 ± 0.2	1.9 ± 0.1	3.8 ± 0.1
	0.5	11.1 ± 0.1	1.7 ± 0.1	3.2 ± 0.1
	1.0	20.6 ± 0.1	2.6 ± 0.1	3.6 ± 0.2
	1.5	29.6 ± 0.1	3.0 ± 0.1	4.2 ± 0.1
Mn	0.1	2.46 ± 0.02	2.7 ± 0.1	4.6 ± 0.1
	0.3	3.64 ± 0.02	2.5 ± 0.1	5.1 ± 0.1
	0.4	8.00 ± 0.05	2.7 ± 0.1	5.5 ± 0.3
	0.5	7.56 ± 0.01	2.8 ± 0.1	5.6 ± 0.3
	1.0	8.18 ± 0.07	3.1 ± 0.2	4.9 ± 0.4
	1.5	24.0 ± 0.1	4.1 ± 0.4	6.1 ± 0.7
Zn	0.1	0.904 ± 0.009	4.7 ± 0.1	7.8 ± 0.1
	0.3	0.364 ± 0.008	2.3 ± 0.1	3.9 ± 0.1
	0.4	0.394 ± 0.001	2.0 ± 0.1	5.3 ± 0.1
	0.5	0.844 ± 0.021	1.5 ± 0.1	3.0 ± 0.2
	1.0	0.934 ± 0.004	1.6 ± 0.01	7.8 ± 0.01
	1.5	2.37 ± 0.01	2.7 ± 0.1	4.2 ± 0.4

[TPPS₄] = 3 μ M; [HCl] = 0.00158 M, T = 298 K